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What is Claimed is:

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1977, 1978, 1979, 1980, 1981, 1982, 1983, 1984, 1985, 1986, 1987, 1988, 1989, 1990, 1991, 1992, 1993, 1994, 1995, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009, 2010, 2011, 2012, 2013, 2014, 2015, 2016, 2017, 2018, 2019, 2020, 2021, 2022, 2023, 2024, 2025, 2026, 2027, 2028, 2029, 2030, 2031, 2032, 2033, 2034, 2035, 2036, 2037, 2038, 2039, 2040, 2041, 2042, 2043, 2044, 2045, 2046, 2047, 2048, 2049, 2050, 2051, 2052, 2053, 2054, 2055, 2056, 2057, 2058, 2059, 2060, 2061, 2062, 2063, 2064, 2065, 2066, 2067, 2068, 2069, 2070, 2071, 2072, 2073, 2074, 2075, 2076, 2077, 2078, 2079, 2080, 2081, 2082, 2083, 2084, 2085, 2086, 2087, 2088, 2089, 2090, 2091, 2092, 2093, 2094, 2095, 2096, 2097, 2098, 2099, 2100, 2101, 2102, 2103, 2104, 2105, 2106, 2107, 2108, 2109, 2110, 2111, 2112, 2113, 2114, 2115, 2116, 2117, 2118, 2119, 2120, 2121, 2122, 2123, 2124, 2125, 2126, 2127, 2128, 2129, 2130, 2131, 2132, 2133, 2134, 2135, 2136, 2137, 2138, 2139, 2140, 2141, 2142, 2143, 2144, 2145, 2146, 2147, 2148, 2149, 2150, 2151, 2152, 2153, 2154, 2155, 2156, 2157, 2158, 2159, 2160, 2161, 2162, 2163, 2164, 2165, 2166, 2167, 2168, 2169, 2170, 2171, 2172, 2173, 2174, 2175, 2176, 2177, 2178, 2179, 2180, 2181, 2182, 2183, 2184, 2185, 2186, 2187, 2188, 2189, 2190, 2191, 2192, 2193, 2194, 2195, 2196, 2197, 2198, 2199, 2200, 2201, 2202, 2203, 2204, 2205, 2206, 2207, 2208, 2209, 2210, 2211, 2212, 2213, 2214, 2215, 2216, 2217, 2218, 2219, 2220, 2221, 2222, 2223, 2224, 2225, 2226, 2227, 2228, 2229, 2230, 2231, 2232, 2233, 2234, 2235, 2236, 2237, 2238, 2239, 2240, 2241, 2242, 2243, 2244, 2245, 2246, 2247, 2248, 2249, 2250, 2251, 2252, 2253, 2254, 2255, 2256, 2257, 2258, 2259, 2260, 2261, 2262, 2263, 2264, 2265, 2266, 2267, 2268, 2269, 2270, 2271, 2272, 2273, 2274, 2275, 2276, 2277, 2278, 2279, 2280, 2281, 2282, 2283, 2284, 2285, 2286, 2287, 2288, 2289, 2290, 2291, 2292, 2293, 2294, 2295, 2296, 2297, 2298, 2299, 2300, 2301, 2302, 2303, 2304, 2305, 2306, 2307, 2308, 2309, 2310, 2311, 2312, 2313, 2314, 2315, 2316, 2317, 2318, 2319, 2320, 2321, 2322, 2323, 2324, 2325, 2326, 2327, 2328, 2329, 2330, 2331, 2332, 2333, 2334, 2335, 2336, 2337, 2338, 2339, 2340, 2341, 2342, 2343, 2344, 2345, 2346, 2347, 2348, 2349, 2350, 2351, 2352, 2353, 2354, 2355, 2356, 2357, 2358, 2359, 2360, 2361, 2362, 2363, 2364, 2365, 2366, 2367, 2368, 2369, 2370, 2371, 2372, 2373, 2374, 2375, 2376, 2377, 2378, 2379, 2380, 2381, 2382, 2383, 2384, 2385, 2386, 2387, 2388, 2389, 2390, 2391, 2392, 2393, 2394, 2395, 2396, 2397, 2398, 2399, 2400, 2401, 2402, 2403, 2404, 2405, 2406, 2407, 2408, 2409, 2410, 2411, 2412, 2413, 2414, 2415, 2416, 2417, 2418, 2419, 2420, 2421, 2422, 2423, 2424, 2425, 2426, 2427, 2428, 2429, 2430, 2431, 2432, 2433, 2434, 2435, 2436, 2437, 2438, 2439, 2440, 2441, 2442, 2443, 2444, 2445, 2446, 2447, 2448, 2449, 2450, 2451, 2452, 2453, 2454, 2455, 2456, 2457, 2458, 2459, 2460, 2461, 2462, 2463, 2464, 2465, 2466, 2467, 2468, 2469, 2470, 2471, 2472, 2473, 2474, 2475, 2476, 2477, 2478, 2479, 2480, 2481, 2482, 2483, 2484, 2485, 2486, 2487, 2488, 2489, 2490, 2491, 2492, 2493, 2494, 2495, 2496, 2497, 2498, 2499, 2500, 2501, 2502, 2503, 2504, 2505, 2506, 2507, 2508, 2509, 2510, 2511, 2512, 2513, 2514, 2515, 2516, 2517, 2518, 2519, 2520, 2521, 2522, 2523, 2524, 2525, 2526, 2527, 2528, 2529, 2530, 2531, 2532, 2533, 2534, 2535, 2536, 2537, 2538, 2539, 2540, 2541, 2542, 2543, 2544, 2545, 2546, 2547, 2548, 2549, 2550, 2551, 2552, 2553, 2554, 2555, 2556, 2557, 2558, 2559, 2560, 2561, 2562, 2563, 2564, 2565, 2566, 2567, 2568, 2569, 2570, 2571, 2572, 2573, 2574, 2575, 2576, 2577, 2578, 2579, 2580, 2581, 2582, 2583, 2584, 2585, 2586, 2587, 2588, 2589, 2590, 2591, 2592, 2593, 2594, 2595, 2596, 2597, 2598, 2599, 2600, 2601, 2602, 2603, 2604, 2605, 2606, 2607, 2608, 2609, 2610, 2611, 2612, 2613, 2614, 2615, 2616, 2617, 2618, 2619, 2620, 2621, 2622, 2623, 2624, 2625, 2626, 2627, 2628, 2629, 2630, 2631, 2632, 2633, 2634, 2635, 2636, 2637, 2638, 2639, 2640, 2641, 2642, 2643, 2644, 2645, 2646, 2647, 2648, 2649, 2650, 2651, 2652, 2653, 2654, 2655, 2656, 2657, 2658, 26

NH(C=O) moiety, wherein when said second functional group is protected, said functional group is deprotected prior to forming said direct or indirect bond, said linker being bonded to the second functional group at the surface of the solid support; and either

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- d) recombining all *M* batches, said recombining step being either prior to or subsequent to step e) and steps e) - g); or
- e) performing an assay capable of indicating that any compound in the library either while bound to or cleaved from its solid support has the property of interest;
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- f) collecting spectral fluorescence data for each respective solid support so as to determine respective relative abundances of the fluorophore tags bound thereto; and
- g) analyzing the collected spectral fluorescence data by comparing the respective relative abundances of the fluorophore tags determined in step
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- f) so as to determine the unique reaction series for the compound, thereby identifying the compound having the property of interest.

2. The method of claim 1 wherein the components are independently selected from the group consisting of an amino acid, a hydroxyacid, an oligoamino acid, an oligopeptide, a saccharide, an oligosaccharide, a diamine, a dicarboxylic acid, an amine-substituted sulfhydryl, a sulfhydryl-substituted carboxylic acid, an alicyclic, an aliphatic, a heteroaliphatic, an aromatic and a heterocyclic moiety.

3. The method of claim 2 wherein the saccharide is a suitably protected D- or L-glucose, fructose, inositol, mannose, ribose, deoxyribose or fucose.

4. The method of claim 2 wherein the oligopeptide is an enkephalin, a vasopressin, an oxytocin, an atrial natrietic factor, a bombesin, a calcitonin, a parathyroid hormone, a neuropeptide Y or an endorphin, or a fragment thereof

comprising at least 20% of the components thereof, or an isosteric analogue thereof wherein independently $\text{NH}(\text{C}=\text{O})$ is replaced by $\text{NH}(\text{C}=\text{O})\text{NH}$, $\text{NH}(\text{C}=\text{O})\text{O}$, $\text{CH}_2(\text{C}=\text{O})$ or CH_2O ; NH_2 is replaced by OH , SH , NO_2 or CH_3 ; CH_3S is replaced by CH_3 ($\text{S}=\text{O}$) or CH_3CH_2 ; indole is replaced by naphthyl or indene; hydroxyphenyl is replaced to tolyl, mercaptophenyl or nitrophenyl; and/or hydrogen in an aromatic ring is replaced by chlorine, bromine, iodine or fluorine; $\text{C}_1\text{-C}_4$ alkyl is replaced by partially or fully fluorinated $\text{C}_1\text{-C}_4$ alkyl.

5. The method of claim 2 wherein the oligopeptide is an ACE inhibitor, an HIV protease inhibitor, a cytolytic oligopeptide or an antibacterial oligopeptide.
6. The method of claim 2 wherein the aromatic is para-disubstituted benzene, biphenyl, naphthalene or anthracene, either substituted or unsubstituted by linear or branched chain lower alkyl, alkoxy, halogen, hydroxy, cyano or nitro.
7. The method of claim 2 wherein the heterocyclic moiety is 2,6-disubstituted pyridine, thiophene, 3-7-disubstituted N-protected indole or 2,4-disubstituted imidazole, either substituted or unsubstituted by linear or branched chain lower alkyl, alkyl, halogen, hydroxy, cyano or nitro.
8. The method of claim 1 wherein the solid support is a microsphere, a bead, a resin or a particle, and is composed of a material selected from the group consisting of polystyrene, polyethylene, cellulose, polyacrylate, polyacrylamide, or preferably a silica to glass bead.
9. The method of claim 1 wherein the solid support is chemically modified by covalent attachment of either a substituted or unsubstituted oligo- or polyethyleneglycol, which either terminated or unterminated by an amine substituted by either hydroxymethyl, chloromethyl, aminomethyl or

mercaptomethyl, wherein the functional group at the surface of the solid support is hydroxy, chlorine, NH_2 or SH , respectively.

10. The method of claim 1 wherein the assay is performed while the compound is cleaved from its solid support under conditions whereby the compound remains adsorbed to the solid support.

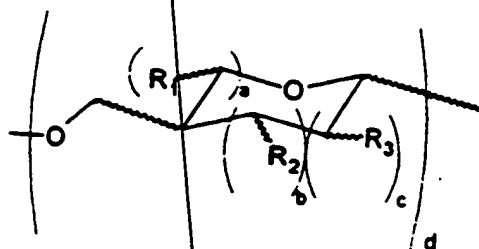
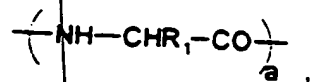
11. The method of claim 1 wherein the property of interest is binding affinity of a compound to a receptor, the assay is performed by determining a physical response to binding by

- a) first admixing with the library of compounds a solution of a labelled receptor so as to result in labelled receptor bound to at least one compound bound to a solid support;
- b) removing the solution from the solid support; and either
- c) washing the solid support so as substantially to remove non-bound labelled receptor, and step (d), or
- d) measuring the physical response due to bound labelled receptor so as to determine the binding affinity.

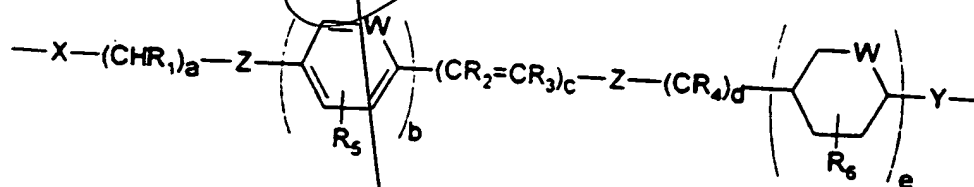
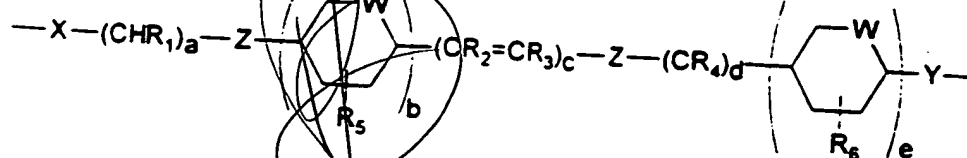
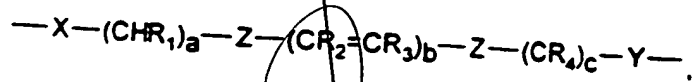
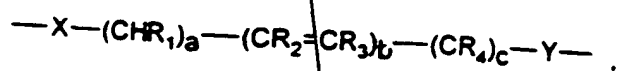
12. The method of claim 11 wherein the receptor is labelled by a fluorescent dye, a colored dye, radioisotope or an enzyme.

13. The method of claim 11 wherein the physical response is fluorescence emission, optical absorption or radioactivity.

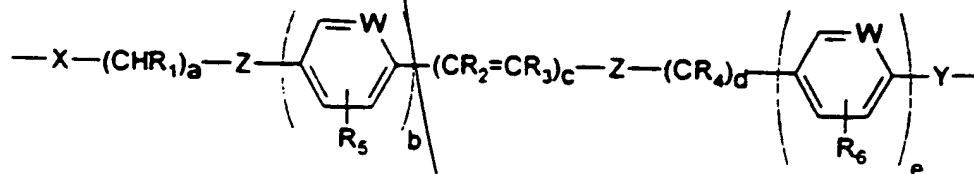
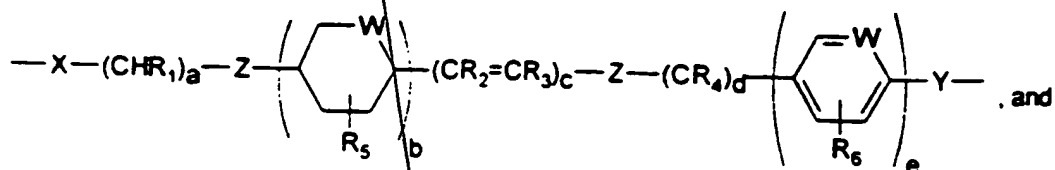
14. The method of claim 1 wherein the components have a structure independently selected from the group consisting of:



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wherein R₁, R₂, R₃, R₄, R₅ and R₆ are independently methyl, ethyl, linear or branched chain C₃-C₉, phenyl, benzyl, benzoyl, cyano, nitro, halo, formyl, acetyl and linear or branched chain C₃-C₉ acyl; wherein a, b, c, d and e are independently 0, 1, 2 or 3; wherein X, Y and Z are independently NH, O, S, S(=O), CO, (CO)O, O(CO), NH(C=O) or (C=O)NH; and wherein W is independently N, O or S.

15. The method of claim 1 wherein at least one component is an amino acid, bearing a protected or unprotected group which is capable of participating in a further reaction or coupling step and is nitrogen, said protecting group being selected from the group consisting of N- α -fluorenylmethyloxycarbonyl, t-butyloxycarbonyl, t-amylloxycarbonyl, (trialkylsilyl) ethyloxycarbonyl, t-butyl and benzyl.
16. The method of claim 1 wherein the fluorophore tag represents a bit of a binary code, and comprises zero, one or more than one fluorescent dye, multiple fluorescent dyes, said dye(s) being spectrally distinguishable by excitation wavelength, emission wavelength, excited-stated lifetime or emission intensity.
17. The method of claim 16 wherein emission intensity is distinguished by adjusting the ration of the relative quantities of each fluorophore.
18. The method of claim 17 wherein the ratio is 1:1, 2:1, 3:1 or 4:1.
19. The method of claim 1 wherein the fluorophore tags are dyes selected from the group consisting of compounds with the chemical names:
3-(ϵ -carboxypentyl)-3'-ethyl-oxacarbocyanine-6,6'-disulfonic acid
1-(ϵ -carboxypentyl)-1'-ethyl-3,3,3',3'-tetramethylindocarbocyanine-5,5'-disulfonic acid

1-(ϵ -carboxypentyl)-1'-ethyl-3,3,3',3'-tetramethyl-3H-

benz(e)indocarbocyanine-5,5',7,7'-tetrasulfonic acid

1-(ϵ -carboxypentyl)-1'-ethyl-3,3,3',3'-tetramethylindocarbocyanine-5,5'-
disulfonic acid

1-(ϵ -carboxypentyl)-1'-ethyl-3,3,3',3'-tetramethyl-3H-

benz(e)indodicarbocyanine-5,5',7,7'-tetrasulfonic acid

1-(ϵ -carboxypentyl)-1'-ethyl-3,3,3',3'-tetramethylindotricarbocyanine-5,5'-
disulfonic acid

and are activated as active esters selected from the group consisting of
succinimidyl, sulfosuccinimidyl, p-nitrophenol, pentafluorophenol, HOBt and
N-hydroxypiperidyl.

20. The method of claim 1 wherein the fluorophore tags are dyes selected from the
group consisting of compounds with the chemical names:

6-((4,4-difluoro-5,7-dimethyl-4-bora-3a,4a-diaza-s-indacene-
3-propionyl)amino) hexanoic acid

6-((4,4-difluoro-5-phenyl-4-bora-3a,4a-diaza-s-indacene-3-propionyl)
amino) hexanoic acid,

6-((4,4-difluoro-1,3-dimethyl-5-(4-methoxyphenyl)-4-bora-3a,
4a-diaza-s-indacene-2-propionyl) amino)hexanoic acid,

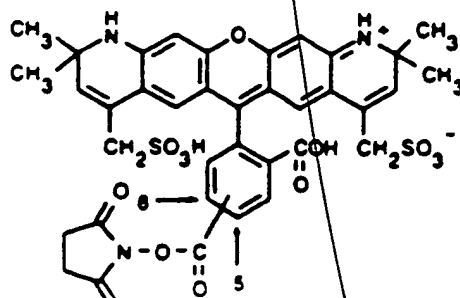
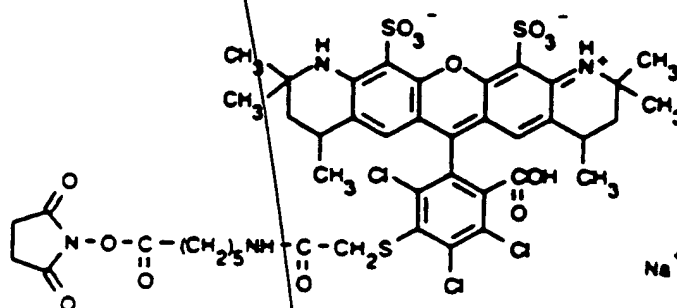
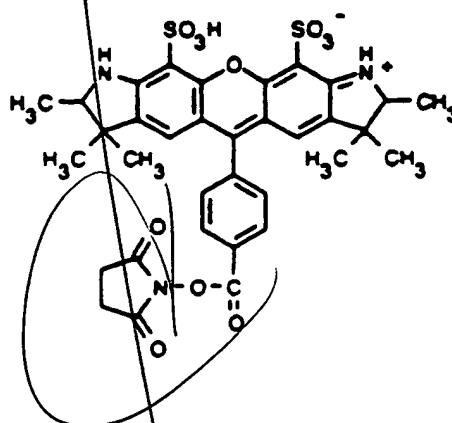
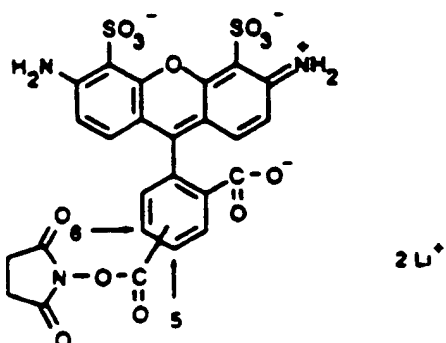
6-(((4,4-difluoro-5-(2-thienyl)-4-bora-3a,4a-diaza-s-indacene-3-yl)
phenoxy) acetyl) amino)hexanoic acid,

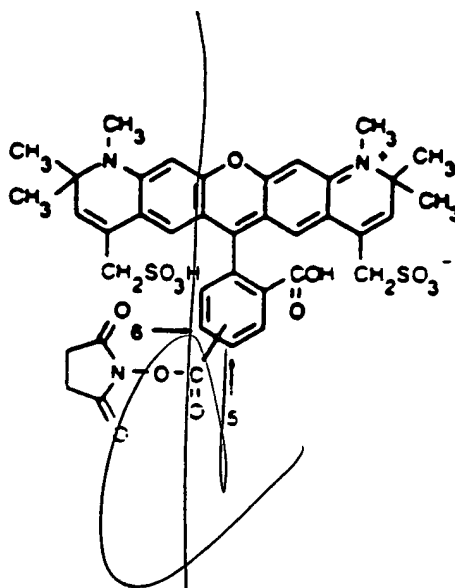
6-(((4,4-difluoro-5-(2-thienyl)-4-bora-3a,4a-diaza-s-indacene-3-yl)
stryloxy)acetyl) aminohexanoic acid, and

6-(((4,4-difluoro-5-(2-pyrrolyl)-4-bora-3a,4a-diaza-s-indacene-3-yl)
stryloxy) acetyl)aminohexanoic acid,

and are activated as active esters selected from the group consisting of
succinimidyl, sulfosuccinimidyl, p-nitrophenol, pentafluorophenol, HOBt and
N-hydroxypiperidyl.

21. The method of claim 1 wherein the fluorophore tags are dyes selected from the group consisting of compounds with the chemical structures:





and are activated as active esters selected from the group consisting of succinimidyl, sulfosuccinimidyl, p-nitrophenol, pentafluorophenol, HOBt and N-hydroxypiperidyl.

22. The method of claim 1 wherein the assay is performed by cleaving compounds from the solid support while permitting diffusion through solution and binding to receptors, said receptors being arranged in proximity to each solid support.
23. The method of claim 1 wherein the fluorescence data are collected from multiple solid supports using multi-spectral imaging methods.
24. The method of claim 1 wherein one of the fluorophore tags uniquely associated with a preselected component or reaction comprises a ligand and a substance capable of binding specifically to the ligand, said ligand being labelled with a fluorophore and attached in a post-assay reaction, said substance being present on the solid support and attached prior to, concurrently with, or subsequent to the coupling of the component, whereby the labelled ligand when bound to the substance indicates the presence of the preselected component.

25. The method of claim 1 wherein the solid support is a polymeric bead, and spectral fluorescence data is collected by
- a) forming either a static planar array or a dynamic planar array of beads; and
 - b) obtaining a fluorescence image for each bead.

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26. The method of claim 25 wherein the planar array of beads is formed adjacent to the planar walls of a sandwich flow cell and controlled by light-controlled electrokinetic means.

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27. The method of claim 25 wherein the planar array of beads is formed by using an apparatus capable of dynamically assembling and disassembling an array of beads at an interface between an electrode and an electrolyte solution, said apparatus comprising:

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- i) an electrode, an electrolyte solution and an interface therebetween
- ii) a plurality of beads located in said electrolyte solutions;
- iii) said electrode being patterned to include at least one area of modified electrochemical properties;
- iv) an illumination source which illuminates said electrode with a predetermined light pattern;
- v) an electric field generator which generates an electric field at said interface to cause the assembly of an array of beads in accordance with the predetermined light pattern and the electrochemical properties of said electrode; and
- vi) an electric field removal unit which removes said electric field to cause the dissembly of said array of beads.

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28. The method of claim 25 wherein spectral fluorescence data are collected for the bead array by initially forming a spatially encoded array of beads

suspended at an interface between an electrode and an electrolyte solution, comprising the following steps:

- i) providing an electrode and an electrolyte solution;
- ii) providing multiple types of particles, each type being stored in accordance with chemically or physically distinguishable particle characteristics in one of a plurality of reservoirs, each reservoir containing a plurality of like-type particles suspended in said electrolyte solution;
- iii) providing said reservoirs in the form of an $m \times n$ grid arrangement;
- iv) patterning said electrode to define $m \times n$ compartments corresponding to said $m \times n$ grid of reservoirs;
- v) depositing $m \times n$ droplets from said $m \times n$ reservoirs onto said corresponding $m \times n$ compartments, each said droplet originating from one of said reservoirs and remaining confined to one of said $m \times n$ compartments and each said droplet containing at least one particle;
- vi) positioning a top electrode above said droplets so as to simultaneously contact each said droplet;
- vii) generating an electric field between said top electrode and said $m \times n$ droplets;
- viii) using said electric field to form a bead array in each of said $M \times N$ compartments, each said bead array remaining spatially confined to one of said $m \times n$ droplets;
- ix) illuminating said $m \times n$ compartments on said patterned electrode with a predetermined light pattern to maintain the position of said bead arrays in accordance with said predetermined light and the pattern of $m \times n$ compartments; and
- x) positioning said top electrode closer to said electrode thereby fusing said $m \times n$ droplets into a continuous liquid phase, while

maintaining each of said $m \times n$ bead arrays in one of the corresponding $m \times n$ compartments.

29. The method of claim 28, wherein said compartments are hydrophilic and the remainder of said electrode surface is hydrophobic.

30. The method of claim 1 wherein N is an integer from at least 2.

31. The method of claim 1 wherein N is an integer from at least 4 to about 12.

32. The method of claim 1 wherein M is an integer from at least 4 to about 10

33. The method of claim 1 wherein from about 0.01 to about 0.05 molar equivalent of a spectrally distinguishable fluorophore tag is added in step c).

34. A compound having a selected property of interest as identified in accord with claim 1.

35. A chemical library prepared in accord with claim 1.

36. An apparatus for identifying a compound having a selected property of interest in a library of compounds, each of said compounds being bound to its respective solid support, and being produced by a unique reaction series composed of N reaction steps, wherein each said compound is prepared from a component, and N is an integer from at least 1 to about 100, said solid support being at least one particle array, said apparatus comprising:

- a) an electrode and an electrolyte solution having an interface therebetween,
- b) an electric field generator which generates an electric field at an interface between an electrode and an electrolyte solution;

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- c) said electrode being patterned to modify the electrochemical properties of said electrode;
- d) an illuminating source which illuminates said interface with a predetermined light pattern to control the movement of said particles in accordance with said predetermined light pattern and the electrochemical properties of said electrode;
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- e) means for preparing said chemical library, which comprises:
- i) means for dividing a population of solid supports having at least one type of a first functional group at the surface of said solid support selected from the group consisting of CO_2H , OH , SH , NH_2 , NHR , CH_2Cl , CH_2Br and CHN_2 , wherein R is a linear $\text{C}_1\text{-C}_9$ alkyl group, into M batches, wherein M is an integer from at least 2 to about 25;
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- ii) means for coupling the M batches of solid support in a set of at least one reaction respectively with M different components so as to form a bond with the solid support via said first functional group, said components being independently protected or unprotected;
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- iii) means for adding to each batch either prior to coupling step ii), concurrently therewith, or subsequently to step ii), from about 0.001 to about 0.5 molar equivalent of a spectrally distinguishable fluorophore tag associated uniquely with each component, said tag being identified by its characteristic excitation wavelength(s), emission wavelength(s), excited state lifetime and emission intensity, said tag being activated so as to be capable of forming
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- either a direct bond to the surface of the solid support, either via the first or a second functional group which is protected or unprotected and is the same as or different from said first functional group, a direct bond to the component which if

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protected is priorly deprotected, or an indirect bond via a C₁-C₉, linear or branched alkyl linker moiety which is either interrupted or uninterrupted by at least one oxygen or nitrogen atom or a carbonyl, (C=O)NH or NH(C=O) moiety, wherein when said second functional group is protected, said second functional group is deprotected prior to forming said direct or indirect bond, said linker being bonded to said second functional group at the surface of the solid support; and either

- iv) means for recombining all *M* batches, said recombining step either being prior to or subsequent to step v), and steps v)-vii); or;
- v) means for performing an assay capable of indicating that any compound in the library either while bound to or cleaved from its solid support has the property of interest;
- vi) means for collecting spectral fluorescence data for each respective solid support so as to determine respective relative abundances of the fluorophore tags bound thereto;
- vii) means for analyzing the collected spectral fluorescence data by comparing the respective relative abundances of the fluorophore tags determined in step vi) so as to determine the unique reaction series for the compound, thereby identifying the compound having the property of interest.

37. A method of identifying a compound having a selected property of interest in a library of compounds, each of said compounds being bound to its respective solid support, and being produced by a unique reaction series composed of *N* coupling or reaction steps, wherein each compound is prepared from components which are independently the same or different, and *N* is an integer from at least 1 to about 100, which comprises:

- 5 a) dividing a population of solid supports having at least one type of a first functional group at the surface of said solid support surface selected from the group consisting of CO_2H , OH , SH , NH_2 , NHR , CH_2Cl , CH_2Br and CHN_2 , wherein R is a linear $\text{C}_1\text{-C}_9$ alkyl group, into M batches, wherein M is an integer from at least 2 to about 50;
- 10 b) coupling the M batches of solid support in a set of at least one reaction respectively with M different initial components so as to form a bond with the solid support via said first functional group, said components being protected or unprotected at a group which is capable of participating in a further coupling step and orthogonally protected at non-participating group(s);
- 15 c) adding to each batch either prior to coupling step b), concurrently therewith, or subsequently to step b), from about 0.001 to about 0.5 molar equivalent of a spectrally distinguishable fluorophore tag associated uniquely with each initial component or a reaction of step b), said tag being identified by its characteristic excitation wavelength(s), emission wavelength(s), excited state lifetime and emission intensity, said tag being activated so as to be capable of forming either a direct bond to the surface of the solid support, either via the first or a second functional group which is protected or unprotected and is the same as or different from said first functional group, a direct bond to the initial component which if protected is priorly deprotected, or an indirect bond via a $\text{C}_1\text{-C}_9$ linear or branched alkyl linker moiety which is interrupted or uninterrupted by either at least one oxygen or nitrogen atom or a carbonyl, $(\text{C}=\text{O})\text{NH}$ or $\text{NH}(\text{C}=\text{O})$ moiety, said linker being bonded to said first functional group at the surface of the solid support, wherein when said second functional group is protected, said second functional group is deprotected prior to forming said direct or indirect bond; and either
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d) recombining all M batches and cleaving any protecting group present at a group which is to participate in a further coupling step, said recombining step being either prior to or subsequent to step e), and steps e)-h); or

e) iteratively $N - 1$ times

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(1) dividing a population of solid supports into $M(N)$ batches, wherein $M(N)$ depends on N and is an integer from at least 2 to about 25;

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(2) coupling the $M(N)$ batches of solid support respectively with $M(N)$ different components, wherein $M(N)$ is the number of batches during the N th step, said components being protected or not protected at a group which is capable of participating in a further coupling step and orthogonally protected at a nonparticipating group(s);

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(3) adding to each batch either prior to coupling step (2), concurrently therewith, or subsequently to step (2), from about 0.001 to about 0.5 molar equivalent of a spectrally distinguishable fluorophore tag associated uniquely with each component in the N th coupling step (2), said tag being identified by its characteristic excitation wavelength(s), emission wavelength(s), excited state lifetime and emission intensity, said tag being activated so as to form either a direct bond to the surface of the solid support, either via a functional group which is protected or not protected and is the same as or different from the functional group bonded to the component, a direct bond to the $(N - 1)$ th component, or an indirect bond via a C_1 - C_n linear or branched alkyl linker moiety which is optionally interrupted by at least one oxygen or nitrogen atom or a carbonyl, $(C=O)NH$ or $NH(C=O)$ moiety, said linker being bonded to the functional group at the surface of the solid support, wherein when said functional group is protected, said

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function group is deprotected prior to forming said direct or indirect bond; and

- (4) recombining all $M(N)$ batches and cleaving any protecting group present at a group which is to participate in a further coupling step;

so as to form a compound having N components;

- f) performing an assay capable of indicating that any compound in the library either while bound to or cleaved from its solid support has the property of interest;
- g) collecting spectral fluorescence data for each respective solid support so as to determine respective relative abundances of the fluorophore tags bound thereto; and
- h) analyzing the collected spectral fluorescence data by comparing the respective relative abundances of the fluorophore tags determined in step g) so as to determine the N components coupled in the unique reaction series for the compound, thereby identifying the compound having the property of interest.

38. The method of claim 37 wherein the components are independently selected from the group consisting of an amino acid, a hydroxyacid, an oligoamino acid, an oligopeptide, a saccharide, an oligosaccharide, a diamine, a dicarboxylic acid, an amine-substituted sulfhydryl, a sulfhydryl-substituted carboxylic acid, an alicyclic, an aliphatic, a heteroaliphatic, an aromatic and a heterocyclic moiety.

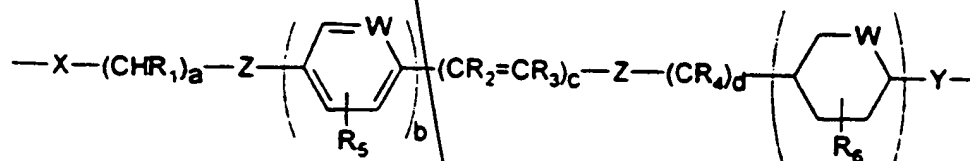
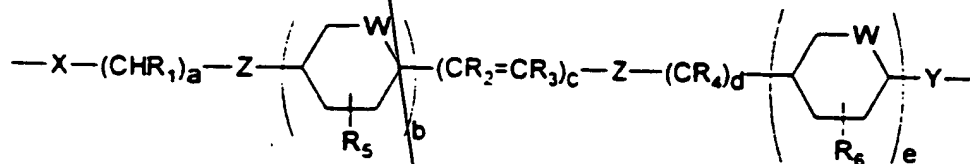
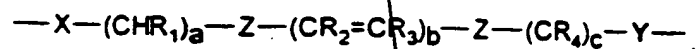
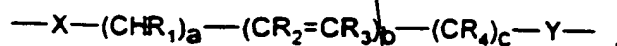
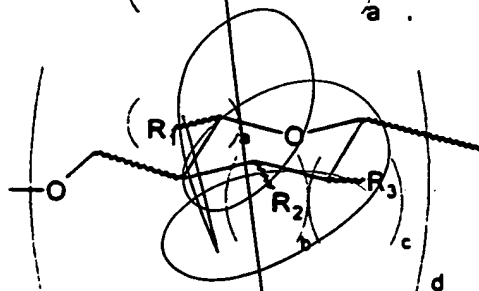
39. The method of claim 38 wherein the saccharide is a suitably protected D- or L-glucose, fructose, inositol, mannose, ribose, deoxyribose or fucose.

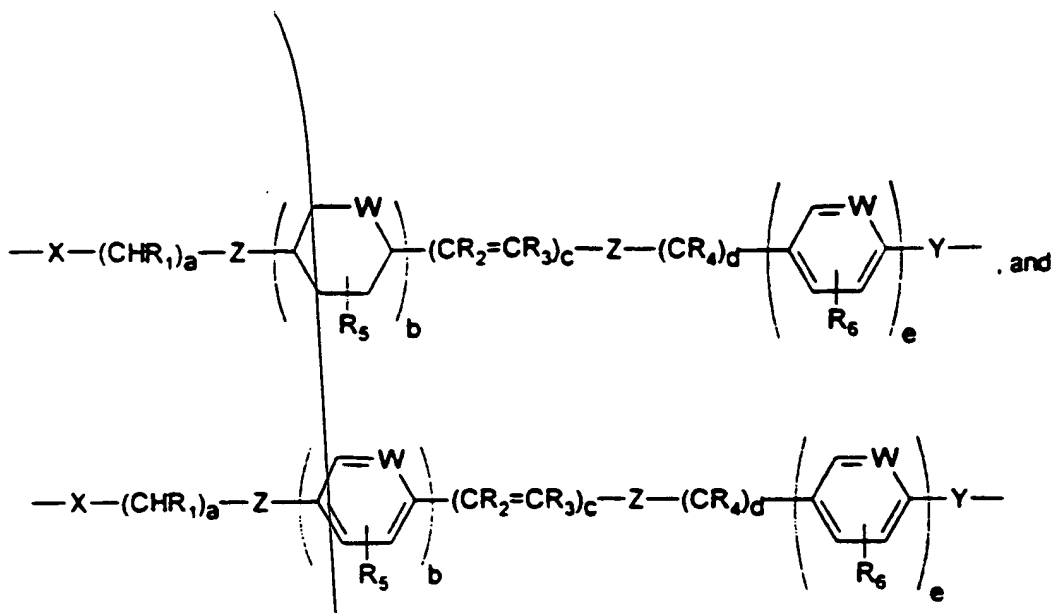
40. The method of claim 38 wherein the oligopeptide is an enkephalin, a vasopressin, an oxytocin, an atrial natrietic factor, a bombesin, a calcitonin, a parathyroid hormone, a neuropeptide Y or an endorphin, or a fragment thereof comprising at least 20% of the components thereof, or an isosteric analogue thereof wherein independently NH(C=O) is replaced by NH(C=O)NH, NH(C=O)O, CH₂(C=O) or CH₂O; NH₂ is replaced by OH, SH, NO₂ CH₃; CH₃ S is replaced by CH₃ (S=O) or CH₃ CH₂; indole is replaced by naphthyl or indene; hydroxyphenyl is replaced by tolyl, mercaptophenyl or nitrophenyl; and/or hydrogen in an aromatic ring is replaced by chlorine, bromine, iodine or fluorine; C₁-C₄ alkyl is replaced by partially or fully fluorinated C₁,-C₄, alkyl.
41. The method of claim 38 wherein the oligopeptide is an ACE inhibitor, an HIV protease inhibitor, a cytolytic oligopeptide or an antibacterial oligopeptide.
42. The method of claim 38 wherein the aromatic is para-di substituted benzene, biphenyl, naphthalene or anthracene, either substituted or unsubstituted by linear or branched chain lower alkyl, alkoxy, halogen, hydroxy, cyano or nitro.
43. The method of claim 38 wherein the heterocyclic moiety is 2,6-disubstituted pyridine, thiophene, 3,7-disubstituted N-protected indole or 2,4-disubstituted imidazole, either substituted or unsubstituted by linear or branched chain lower alkyl, alkoxy, halogen, hydroxy, cyano or nitro.
44. The method of claim 37 wherein the solid support is a microsphere, a bead, a resin or a particle, and is composed of a material selected from the group consisting of polystyrene, polyethylene, cellulose, polyacrylate, polyacrylamide, or preferably a silica or glass bead.

45. The method of claim 37 wherein the solid support is chemically modified by covalent attachment of a substituted or unsubstituted oligo- or polyethyleneglycol, which is either terminated or unterminated by an amine substituted by either hydroxymethyl, chloromethyl, aminomethyl or mercaptomethyl, wherein the functional group at the surface of the solid support is hydroxy, chlorine, NH_2 or SH , respectively.
46. The method of claim 37 wherein the assay is performed while the compound is attached to its solid support.
47. The method of claim 37 wherein the assay is performed while the compound is cleaved from its solid support under conditions whereby the compound remains adsorbed to the solid support.
48. The method of claim 37 wherein when the property of interest is binding affinity of a compound to a receptor, the assay is performed by determining a physical response to binding by
- a) first admixing with the library of compounds a solution of a labelled receptor so as to result in labelled receptor bound to at least one compound bound to a solid support;
 - b) removing the solution from the solid support; and either
 - c) washing the solid support so as substantially to remove non-bound labelled receptor, and step (d); or
 - d) measuring the physical response due to bound labelled receptor so as to determine the binding affinity.
49. The method of claim 48 wherein receptor is labelled by a fluorescent dye, a colored dye, radioisotope or an enzyme.

50. The method of claim 48 wherein the physical response is fluorescence emission, optical absorption or radioactivity.

51. The method of claim 37 wherein the components have a structure independently selected from the group consisting of:





wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are independently methyl, ethyl, linear or branched chain C_3 - C_9 alkyl, phenyl, benzyl, benzoyl, cyano, nitro, halo, formyl, acetyl and linear or branched chain C_3 - C_9 acyl; wherein a , b , c , d and e are independently 0, 1, 2 or 3; wherein X , Y and Z are independently NH, O, S, S(=O), CO, (CO)O, O(CO), NH(C=O) or (C=O) NH; and wherein W is independently N, O or S.

52. The method of claim 37 wherein at least one component is an amino acid, and the protected or unprotected group which is to participate in a further coupling step is nitrogen, said protecting group being selected from the group consisting of *N*- α -fluorenylmethyloxycarbonyl, *t*-butyloxcarbonyl, *t*-amyloxycarbonyl, (trialkylsilyl) ethyloxycarbonyl, *t*-butyl and benzyl;
53. The method of claim 37 wherein the fluorophore tag represents a bit of binary code, and comprises zero, one or more than one fluorescence dye, multiple fluorescent dyes, said dye(s) being spectrally distinguishable by excitation wavelength, emission wavelength, excited-state lifetime or emission intensity.

54. The method of claim 37 wherein the assay is performed by cleaving compounds from the solid support while permitting diffusion through solution and binding to receptors, said receptors being arranged in proximity to each solid support.

55. The method of claim 37 wherein the fluorescence data are collected from multiple solid supports using multi-spectral imaging methods.

56. The method of claim 53 wherein emission intensity is distinguished by adjusting the ratio of the relative quantities of each fluorophore.

57. The method of claim 56 wherein the ratio is 1:1, 2:1, 3:1 or 4:1.

58. The method of claim 37 wherein the fluorophore tags are dyes selected from the group consisting of compounds with the chemical names:

3-(ϵ -carboxypentyl)-3'-ethyl-oxacarbocyanine-6,6'-disulfonic acid

1-(ϵ -carboxypentyl)-1'-ethyl-3,3,3',3'-tetramethylindocarbocyanine-5,5'-disulfonic acid

1-(ϵ -carboxypentyl)-1'-ethyl-3,3,3',3'-tetramethyl-3H-benz(e)indocarbocyanine-5,5',7,7'-tetrasulfonic acid

1-(ϵ -carboxypentyl)-1'-ethyl-3,3,3',3'-tetramethylindocarbocyanine-5,5'-disulfonic acid

1-(ϵ -carboxypentyl)-1'-ethyl-3,3,3',3'-tetramethyl-3H-benz(e)indodicarbocyanine-5,5',7,7'-tetrasulfonic acid

1-(ϵ -carboxypentyl)-1'-ethyl-3,3,3',3'-tetramethylindotricarbocyanine-5,5'-disulfonic acid

and are activated as active esters selected from the group consisting of succinimidyl, sulfosuccinimidyl, p-nitrophenol, pentafluorophenol, HOBt and N-hydroxypiperidyl

59. The method of claim 37 wherein the fluorophore tags are dyes selected from the group consisting of compounds with the chemical names:

6-((4,4-difluoro-5,7-dimethyl- 4-bora-3a,4a-diaza-s-indacene-3-propionyl)amino) hexanoic acid

6-((4,4-difluoro-5-phenyl-4-bora-3a,4a-diaza-s-indacene-3-propionyl) amino) hexanoic acid.

6-((4,4-difluoro-1,3-dimethyl-5-(4-methoxyphenyl)-4-bora-3a,
4a-diaza-s-indacene- 2-propionyl) amino)hexanoic acid,

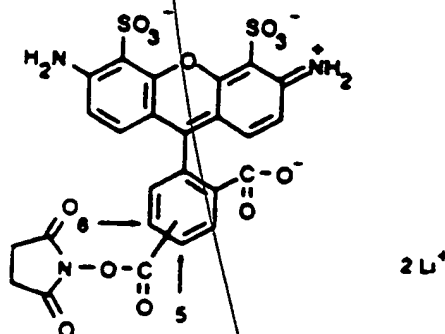
6-(((4-(4,4-difluoro-5-(2-thienyl)-4-bora-3a,4a-diaza-s-indacene-3-yl)phenoxy) acetyl) amino)hexanoic acid,

6-(((4,4-difluoro-5-(2-thienyl)-4-bora-3a,4a-diaza-s-indacene-3-yl)styryloxy)acetyl) aminohexanoic acid, and

6-(((4,4-difluoro-5-(2-pyrrolyl)-4-bora-3a,4a-diaza-s-indacene-3-yl)styryloxy) acetyl)aminohexanoic acid.

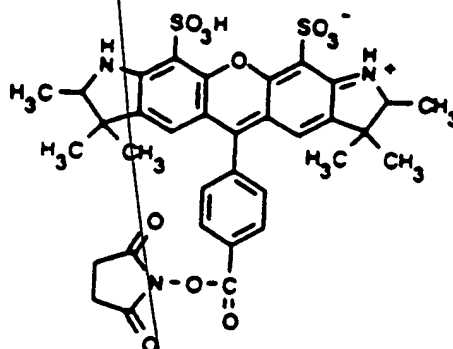
and are activated as active esters selected from the group consisting of succinimidyl, sulfosuccinimidyl, p-nitrophenol, pentafluorophenol, HOBt and N-hydroxypiperidyl.

60. The method of claim 37 wherein the fluorophore tags are dyes selected from the group consisting of compounds with the chemical structures:

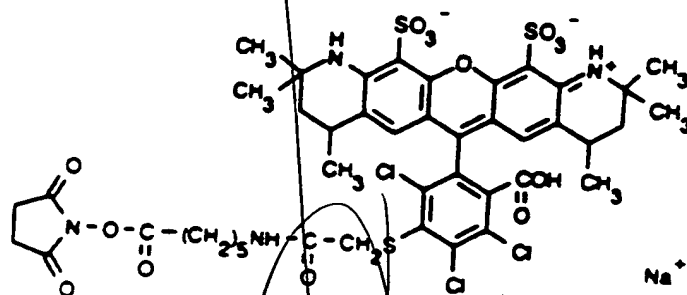


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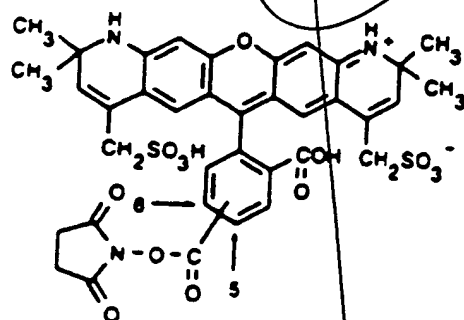
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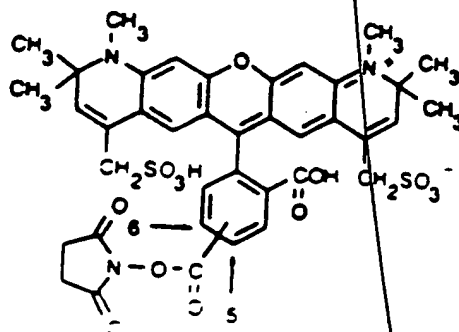


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and are activated as active esters selected from the group consisting of succinimidyl, sulfosuccinimidyl, p-nitrophenol, pentafluorophenol, HOBt and N-hydroxypiperidyl.

- 5 61. The method of claim 37 wherein one of the fluorophore tags uniquely associated with a preselected component or reaction comprises a ligand and a substance capable of binding specifically to the ligand, said ligand being labelled with a fluorophore and attached in a post-assay reaction, said substance being present on the solid support and attached prior to, concurrently with, or subsequent to the coupling of the component, whereby the labelled ligand when bound to the substance indicates the presence of the preselected component.
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- 15 62. The method of claim 37 wherein the solid support is a bead, and spectral fluorescence data are collected by
- a) forming either a static planar array or a dynamic planar array of beads; and
 - b) obtaining a fluorescence image for at least one bead.
- 20 63. The method of claim 62 wherein the planar array of beads is formed adjacent to the planar walls of a sandwich flow cell and controlled by light-controlled electrokinetic means.
- 25 64. The method of claim 62 wherein the dynamic planar array of beads is formed by using an apparatus capable of dynamically assembling and disassembling an array of beads at an interface between an electrode and an electrolyte solution, said apparatus comprising:
- i) an electrode, an electrolyte solution and an interface there between;
 - ii) a plurality of beads located in said electrolyte solution;

- iii) said electrode being patterned to include at least one area of modified electrochemical properties;
- iv) an illumination source which illuminates said electrode with a predetermined light pattern;
- 5 v) an electric field generator which generates an electric field at said interface to cause the assembly of an array of beads in accordance with the predetermined light pattern and the electrochemical properties of said electrode; and
- vi) an electric field removal unit which removes said electric field to cause the disassembly of said array of beads.

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65. The method of claim 62 wherein spectral fluorescence data are collected for the bead array by initially forming a spatially encoded array of beads suspended at an interface between an electrode and an electrolyte solution, comprising the following steps:

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- i) providing an electrode and an electrolyte solution;
- ii) providing multiple types of particles, each type being stored in accordance with chemically or physically distinguishable particle characteristics in one of a plurality of reservoirs, each reservoir containing a plurality of like-type particles suspended in said electrolyte solution;
- 20 iii) providing said reservoirs in the form of an $m \times n$ grid arrangement;
- iv) patterning said electrode to define $m \times n$ compartments corresponding to said $m \times n$ grid of reservoirs;
- 25 v) depositing $m \times n$ droplets from said $m \times n$ reservoirs onto said corresponding $m \times n$ compartments, each said droplet originating from one of said reservoirs and remaining confined to one of said $m \times n$ compartments and each said droplet containing at least one particle;

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- vi) positioning a top electrode above said droplets so as to simultaneously contact each said droplet;
- vii) generating an electric field between said top electrode and said *mxn* droplets;
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- viii) using said electric field to form a bead array in each of said *mxn* compartments, each said bead array remaining spatially confined to one of said *mxn* droplets;
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- ix) illuminating said *mxn* compartments on said patterned electrode with a predetermined light pattern to maintain the position of said bead arrays in accordance with said predetermined light pattern and the pattern of *mxn* compartments; and
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- x) positioning said top electrode closer to said electrode thereby fusing said *mxn* droplets into a continuous liquid phase, while maintaining each of said *mxn* bead arrays in one of the corresponding *mxn* compartments.
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66. The method of claim 65 wherein said compartments are hydrophilic and the remainder of said electrode surface is hydrophobic.

20 67. The method of claim 37 wherein *N* is an integer from at least 3 to about 12.

68. The method of claim 37 wherein *M* and *M(N)* are independently an integer from at least 4 to about 12.

25 69. The method of claim 37 wherein from about 0.01 to about 0.05 molar equivalent of a spectrally distinguishable fluorophore tag is added in step c).

70. A compound having a selected property of interest as identified in accord with claim 37.

71. A chemical library prepared in accord with claim 37.

72. An apparatus for identifying a compound having a selected property of interest in a library of compounds, each of said compounds being bound to its respective solid support, and being produced by a unique reaction series composed of N coupling and reaction steps, wherein each said compound is prepared from a set of components which are independently the same or different, and N is an integer from at least 1 to about 100, said solid support being at least one particle array, said apparatus comprising:

- a) an electrode and an electrolyte solution having an interface therebetween;
- b) an electric field generator which generates an electric field at an interface between an electrode and an electrolyte solution;
- c) said electrode being patterned to modify the electrochemical properties of said electrode;
- d) an illuminating source which illuminates said interface with a predetermined light pattern to control the movement of said particles in accordance with said predetermined light pattern and the electrochemical properties of said electrode;
- e) means for preparing said chemical library, which comprises:
 - i) means for dividing a population of solid supports having at least one type of a first functional group at the surface of said solid support selected from the group consisting of CO_2H , OH , SH , NH_2 , NHR , CH_2Cl , CH_2Br and CHN_2 , wherein R is a linear C_1 - C_9 alkyl group, into M batches, wherein M is an integer from at least 2 to about 50;
 - ii) means for coupling the M batches of solid support in a set of at least one reaction respectively with M different initial components so as to form a bond with the solid support via said first functional group, said components being protected or unprotected at a group which is

to participate in a further coupling step and orthogonally protected at non-participating group(s);

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iii) means for adding to each batch either prior to coupling step ii), concurrently therewith, or subsequently to step ii), from about 0.001 to about 0.5 molar equivalent of a spectrally distinguishable fluorophore tag associated uniquely with each initial component, said tag being identified by its characteristic excitation wavelength(s), emission wavelength(s), excited state lifetime and emission intensity, said tag being activated so as to be capable of forming either a direct bond to the surface of the solid support, either via the first or a second functional group which is protected or unprotected and is the same as or different from said first functional group bonded to the component, or an indirect bond via a C₁-C₉, linear or branched alkyl linker moiety which is either interrupted or uninterrupted by either at least one oxygen or nitrogen atom or a carbonyl, (C=O)NH or NH(C=O) moiety, said linker being bonded to said second functional group at the surface of the solid support, wherein when said second functional group is protected, said second functional group is deprotected prior to forming said direct or indirect bond; and either

iv) means for recombining all *M* batches and cleaving any protecting group present at a group which is to participate in a further coupling step, and steps v)-viii); or

v) means for iteratively *N* - 1 times

(1) dividing a population of solid supports into *M(N)* batches, wherein *M(N)* depends on *N* and is an integer from at least 2 to about 25;

(2) coupling the *M(N)* batches of solid supports respectively with *M(N)* different components, wherein *M(N)* is the number of

batches during the N th step, said components being protected or unprotected at a group which is capable of participating in a further coupling step and orthogonally protected at a non-participating group(s);

- 5 (3) adding to each batch either prior to coupling step (2), concurrently therewith, or subsequently to step (2), from about 0.001 to about 0.1 molar equivalent of a different spectrally distinguishable fluorophore tag associated uniquely with each component during the N th coupling step (2), said tag being uniquely identified by its excitation wavelength, emission wavelength, excited-state lifetime or emission intensity, whereby said tag is activated so as to be capable of forming either a direct bond to the solid support, either via an N th functional group which is protected or unprotected and is the same as or different from the first functional group, or an indirect bond thereto via a C_1 - C_9 linear or branched alkyl linker moiety which is either interrupted or uninterrupted by either at least one oxygen or nitrogen atom or a carbonyl or $NH(C=O)$ moiety, or a direct bond to the $(N-1)$ th component which if protected is priorly deprotected, said tag or linker being bound via the group which is to participate in a further coupling step, wherein when said N th functional group is protected, said N th functional group is deprotected prior to forming said direct or indirect bond; and
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- 25 (4) recombining all $M(N)$ batches and cleaving the protecting group present if present at a group which is to participate in a further coupling step;

so as to form a compound having N components;

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- vi) means for performing an assay capable of indicating that any compound in the library either while bound to or cleaved from its solid support has the property of interest;
- vii) means for collecting spectral fluorescence data for each respective solid support so as to determine respective relative abundances of the fluorophore tags bound thereto;
- viii) means for analyzing the collected spectral fluorescence data by comparing the respective relative abundances of the fluorophore tags determined in step vii) so as to determine the N components coupled in the unique reaction series for the compound, thereby identifying the compound having the selected property of interest.

Sub
A₅

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collect "data"

A₀₀
A₁

add
01

add
02